SYNTHESIS AND EVALUATION OF AMINOBORATES DERIVED FROM BORIC ACID AND DIOLS FOR PROTECTING WOOD AGAINST FUNGAL AND THERMAL DEGRADATION[1]

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(Received June 2007)

Abstract. N-methyl amino catechol borate (1), N-methyl amino-4-methyl catechol borate (2), N-methyl amino-4-t-butyl catechol borate (3), and N-methyl amino-2, 3-naphthyl borate (4) were synthesized by reflux of boric acid with a diol in solvent N,N-dimethyl formamide. The aminoborates were characterized by proton nuclear magnetic resonance spectroscopy, FTIR spectroscopy and elemental analysis. Wood impregnated with aminoborate 1, 3, or 4 after 2-wk water leaching was able to prevent decay by a brown- and white-rot fungus. Thermogravimetric analysis showed that wood impregnated with aminoborate 1 or 4 had a high char yield. DSC showed that the pyrolysis pathway of wood treated with aminoborates proceeds by depolymerization of cellulose. Chars formed from wood impregnated with aminoborates were more stable to thermal degradation than the control.

Keywords: Aminoborates, fungal decay, thermal protection, synthesis, wood.

INTRODUCTION

The degradation of wood by decay, insects, fire, and UV radiation constitutes the four major losses of wood products in use. If achievable, dual protection of wood against decay and fire, or decay and UV is desirable. Many phosphorus and boron compounds possess fire-retardant and decay-resistant properties. In our previous investigations (Lee et al 2004a 2004b), we found that wood reacted with phosphoramidates produced in situ by reacting phosphorus pentoxide with amines can protect wood from fungal decay and thermal degradation. The purpose of this research was to synthesize low water-soluble aminoborates and evaluate fungal decay and thermal protection in wood.

MATERIALS AND METHODS

Synthesis and characterization

We attempted to synthesize a biborate A (Fig 1) by reflux of a stoichiometric amount of boric acid with catechol in DMF (N, N-dimethyl formamide). However, the product after 1-h reflux was not a biborate but an aminoborate 1 (Fig 2). The aminoborate was formed as a result of condensation of catechol borate with solvent DMF.

Other aminoborates (aminoborate 2, 3, and 4) can be synthesized from aromatic diols, including 4-methyl catechol, 4-t-butyl catechol, and 2, 3-dihydroxy naphthalene, with boric acid in DMF (Fig 2). The aminoborates can be synthesized from aromatic diols containing electron-donating methyl and t-butyl groups. Attempts to synthesize aminoborates from aromatic diols containing electron-withdrawing aldehydric, nitro, and carboxyl groups with boric acid in DMF were unsuccessful. The aminoborates have very low water solubility, and are insoluble in most organic solvents except DMF and dimethyl sulf-

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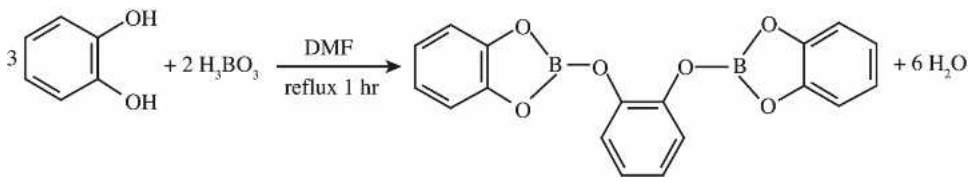

FIGURE 1. Synthesis of biborate A

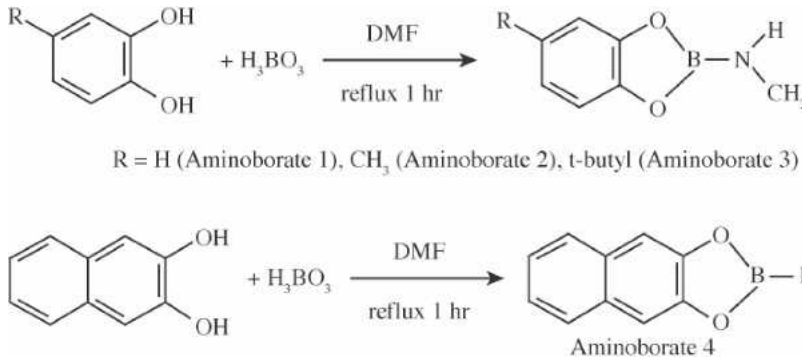

FIGURE 2. Synthesis of aminoborates

oxide (DMSO). The aminoborates can be crystallized from DMF and methanol. A general procedure for synthesis of aminoborates is described below.

Aromatic diol (0.1 mol) and boric acid (6.2 g, 0.1 mol) dissolved in DMF (25 mL, dried over molecular sieve 4-A° for more than 1 da) were under reflux in dry atmosphere for 1 h After 30 min reflux, an insoluble solid appeared in the solution. The solution was evaporated to dryness to form a solid. The solid was triturated with acetone (50 mL), and the acetone-insoluble solid was recovered by filtration to give a white solid. The solid can be crystallized from hot methanol or DMF. The crystals did not melt when heated to 210°C. Yields of aminoborates were listed below: aminoborate 1 (62%), aminoborate 2 (58%), aminoborate 3 (50%), and aminoborate 4 (78%).

IR absorption of aminoborates was determined by a Galaxy Series FTIR 5000 (Unicam, England) spectrophotometer using KBr. Proton NMR (^{1}HNMR) of aminoborates was determined by an Avance DPX 250 NMR (Bruker BioSpin Corporation, Billerica, MA) instrument using d_6-DMSO as a solvent.

Elemental analysis of aminoborates was performed by the Galbraith Laboratories, Inc., (Knoxville, TN) using Inductively Coupled Plasma (ICP)–Atomic Emission Spectroscopy (AES) method for boron analysis.

Fungal decay evaluation

Fourteen loblolly pine (*Pinus taeda* L.) or sweet gum (*Liquidambar styraciflua L.)* sapwood blocks (19 mm in radial, tangential, and longitudinal directions) in a 0.47-L bottle were placed under a vacuum at 2.1–3.3 kPa for 30 min in a desiccator and then impregnated with DMF solutions of aminoborates as well as aqueous solutions of boric acid at four concentration levels: 1.6, 11.2, 22.4, and 44.8 mmol/100 g solution for boric acid; 1.4, 9.6, 19.2, and 38.4 mmol/100 g wood for aminoborate 1 and 2, and 1.4, 9.9, 19.8, and 39.7 mmol/100 g wood for aminoborate 3 and 4. The blocks were soaked for 1 da. After soaking, the blocks were dried in a chemical fume hood for 3 da and then heated in an

oven at 105°C for 2 da. Half of the blocks (7 blocks per treatment) were conditioned at 27°C and 30% relative humidity (RH) for 3 wk. Another 7 blocks per treatment were leached in 350 mL distilled water 6, 24, and 48 h and then every 24 h for 2 wk according to the American Society for Testing Materials (ASTM) procedure, section 12.2 (ASTM 2000). After leaching, the blocks were also conditioned at 27°C and 30% RH for 3 wk.

Soil-block fungal decay tests were carried out according to ASTM standards (ASTM 2000). *Gloeophyllum trabeum* (Pers.:Fr.) Murr., MAD-617, a brown-rot fungus was used with pine blocks, and *Trametes versicolor* (L.:Fr.) Quel., MAD-697, a white-rot fungus was used with sweet gum blocks. Five replicate blocks from each treatment, 5 control and 5 blocks treated with solvent alone were tested for decay resistance for 12 wk. The extent of fungal attack was determined by weight loss. Chemical retention was determined by weight gain of treated wood blocks multiplied by the solution concentration and expressed as mmol chemical/100 g wood. The solution concentration was expressed as mmol/100 g solution. Threshold retention was determined by the intercept of operational weight loss line and operational weight loss plus decay loss line according to ASTM D 1413–99 section 17.1 (ASTM 2000). These two lines were obtained from logarithmic curves. Where there was decay loss line only, the threshold retention was estimated at 2% weight loss by logarithmic scale.

Thermal properties evaluation

Loblolly pine wood treated with aminoborates or boric acid and diammonium phosphate at 100 mmol per 100 g wood was analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Five mg of specimen were used. For TGA, samples were analyzed by a Perkin Elmer TGA 7 (PerkinElmer Life and Analytical Sciences, Inc., Waltham, MA). Derivative thermal gravimetric analysis (DTG) provided a rate of mass loss as a function of temperature and time. Char residue, maximum temperature of pyrolysis, and rate of weight loss were obtained from TGA and DTG.

The above samples were also analyzed by a Perkin Elmer DSC 7. Five mg of sample were heated under nitrogen from 50–500°C with nitrogen flow rate of 20 mL/min and heating rate of 10°C/min. Pyrolysis of wood components and wood by DSC in Fig 5 was taken from our previous paper (Lee et al 2004a). Wood components including cellulose, xylan, and lignin were obtained from Aldrich Chemical Company.

RESULTS AND DISCUSSION

Elemental analysis

The elemental analysis of aminoborate 1 showed that boron and hydrogen were close to the theoretical values, whereas carbon deviated from the theoretical value (Table 1). The aminoborates after recrystalization always contained a trace of impurities as shown by thin layer chromatography using silica gel 60 F_{254} precoated plastic sheets with methanol or acetone as a developing solvent. Because of difficulty in obtaining a pure compound, no boron analysis was made for aminoborate 2, 3, and 4.

Proton NMR

Proton NMR showed that all four aminoborates have methyl protons of the amino group in the

TABLE 1. *Elemental analysis of aminoborates.*

	Theoretical			Found		
Compound	C	H	B	C	H	B
Aminoborate 1: ($C_6H_4O_2BNHCH_3$)	56.44	5.40	7.26	53.49	5.66	6.96
Aminoborate 2: ($CH_3C_6H_3O_2BNHCH_3$)	58.96	6.64		62.97	6.62	a
Aminoborate 3: ($(CH_3)_3C_6H_3O_2BNHCH_3$)	64.43	7.86		67.39	8.35	a
Aminoborate 4: ($C_{10}H_6O_2BNHCH_3$)	66.38	5.06		70.35	5.27	a

a No boron analysis was made.

molecule. This indicated that solvent DMF was participating in the reaction through condensation of solvent with diol borates. No reports were found in the literature regarding the synthesis of alkylaminoborates from reaction of catechol or aromatic diol borates with alkylamines. However, in our continuing investigations of aminoborates, we were able to synthesize low water-soluble dialkyl aminoborates from boric acid and dialkyl amines including dihexylamine and dioctylamine. The mechanism of reaction is not clear but may involve initial nucleophilic substitution of OH of catechol borate by solvent DMF and subsequent elimination of aldehydric and methyl groups from DMF to form acetic acid as a by-product and aminoborate as a major product.

Proton NMR of aminoborates (Fig 3, Table 2) in d_6-DMSO and chemical shifts expressed in ppm showed the characteristic methyl protons of the amino group at 2.5−2.55 ppm for four aminoborates, methyl protons of the aromatic group of aminoborate 2 at 2.2 ppm, methyl protons of the t-butyl group of aminoborate 3 at 1.2 ppm, aromatic protons of four aminoborates at 6.25−7.8 ppm, and amino proton at 8.2 ppm. Detail assignments of protons for aromatic groups are shown in Table 2.The integration of amino proton for aminoborate 2 and 4 was lower. This may be attributed to the amino proton being able to exchange with solvent d_6-DMSO.

IR absorption of aminoborates (Fig 4) showed strong IR absorption at 1,478−1,501 cm^{-1}, which was attributed to B-N stretching vibration (Colthup et al 1964; Socrates 1994). For aminoborate 1, this absorption appeared at 1,489 cm^{-1}, aminoborate 2 at 1,501 cm^{-1}, aminoborate 3 at 1,497 cm^{-1} and aminoborate 4 at 1,478 cm^{-1}.

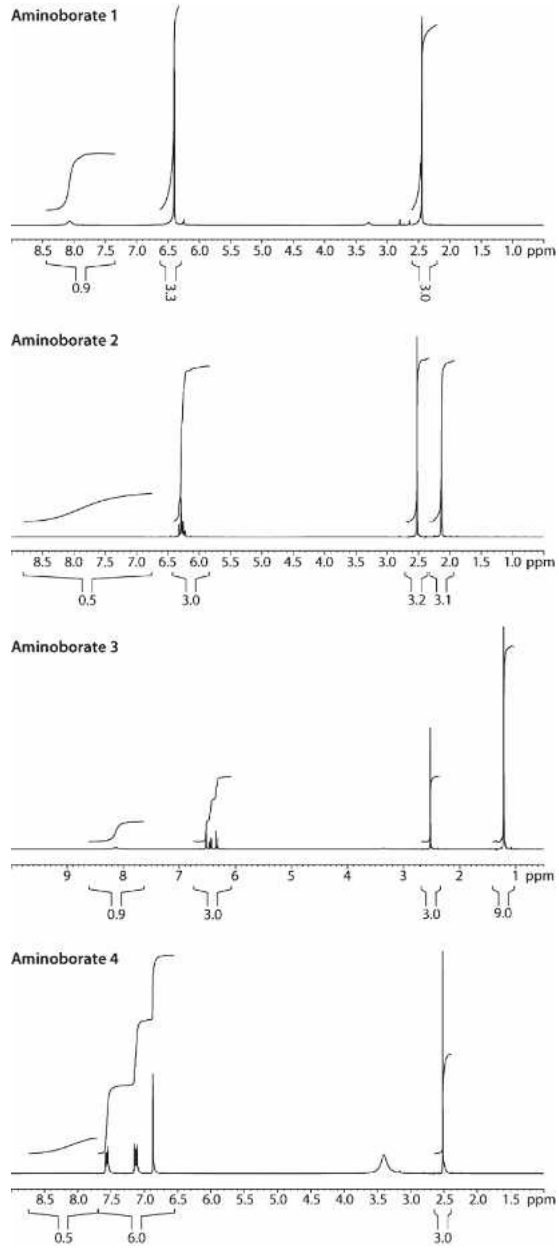

FIGURE 3. Proton NMR spectra of aminoborate 1, 2, 3 and 4.

Fungal decay evaluation

Brown-rot fungus. Weight losses of aminoborate-treated pine wood decayed by *G. trabeum* are shown in Table 3. For pine wood impregnated with aminoborate 1, threshold retention with *G. trabeum* was 3 mmol/100 g wood for nonleached and 9.6 mmol/100 g wood for leached blocks. Weight losses were 1.6% for nonleached and 1.9% for leached wood for chemical retention of 10.2 mmol/100 g wood. Leaching decreased the decay resistance. For aminoborate 2, threshold retention with *G. tra-*

TABLE 2. *Proton NMR (^1H NMR) spectra of aminoborates in d_6-DMSO.*

Aminoborates	Methyl protons (ppm)	Aromatic protons (ppm)	Amino proton (ppm)
Aminoborate 1	2.5 (s,3H,methyl protons of amino group)	6.45 (s,4H,aromatic C3,C4,C5,C6 protons)	8.2 (s,1H)
Aminoborate 2	2.2 (s,3H,methyl protons of aromatic group); 2.55 (s,3H,methyl protons of amino group)	6.25–6.3 (m,3H,aromatic C3,C5,C6 protons)	8.2 (s,1H)
Aminoborate 3	1.2 (s,9H,methyl protons of t-butyl group); 2.5 (s,3H, methyl protons of amino group)	6.3,6.4,6.5(d,3H,aromatic C6,C3,C5 protons)	8.2 (s,1H)
Aminoborate 4	2.5 (s,3H,methyl protons of amino group)	6.8 (s,2H,C3,C10 protons of napthyl group), 7.2 (d,2H,C5,C8 protons of napthyl group), 7.8 (d,2H,C6,C7 protons of napthyl group)	8.2 (s,1H)

s: singlet; d: doublet; m: multiplet.

beum was 9.8 mmol/100g wood for nonleached blocks. Weight losses for chemical retention at 10.1 mmol/100 g wood was 1.4% for nonleached wood and threshold retention was not reached for leached blocks. For aminoborate 3, threshold retention with *G. trabeum* was below 1.5 mmol/100 g wood for nonleached blocks. Weight loss for chemical retention at 1.5 mmol/100 g wood was 0.7% for nonleached wood. For leached wood, threshold retention was 22.5 mmol/100 g wood. Weight loss was 0% at retention of 43.6 mmol/100 g wood for leached wood. Leaching decreased the decay resistance. For aminoborate 4, threshold retentions with *G. trabeum* was 8.4 mmol/100 g wood for nonleached blocks. Weight loss was 0.6% at retention of 10.4 mmol/100 g wood for nonleached wood. For leached blocks, threshold retention was 18 mmol/100 g wood. Weight loss was 0.7% at retention of 21.4 mmol/100 g wood for leached wood. Leaching decreased the decay resistance. The control had 27.4% weight loss, and blocks treated with solvent DMF alone had 23.7% weight loss. Blocks treated with solvent alone are required to dry at 105°C for 2 da to avoid the effect of solvent on decay tests.

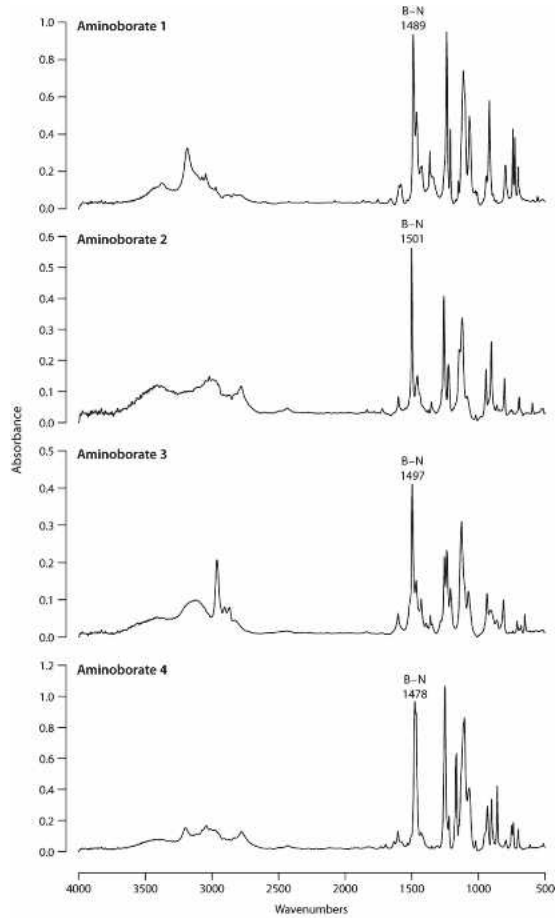

FIGURE 4. FTIR spectra of aminoborate1, 2, 3 and 4.

The above decay tests showed that aminoborate 1, 2, 3, and 4 in wood without leaching were as effective as boric acid against *G. trabeum*. For nonleached blocks, threshold retentions ranged from 1.5–9.8 mmol/100 g wood, whereas boric acid was 10.6 mmol/100 g wood. For aminoborate 1, leaching slightly decreased the decay resistance to threshold retention of 9.6 mmol/100 g wood, but for aminoborate 4 and 3, leaching decreased decay resistance. Threshold retentions

TABLE 3. *Effect of aminoborates on weight losses of pine blocks decayed by* Gloeophyllum trabeum *in a 12-wk soil-block fungal decay test.*

Treatment	Solution concentration (mmol/100 g solution)	Chemical retention (mmol/100 g content wood)[a]	Boron (%)	Weight loss (%)[b] by *Gt*	
				Non-leached	Leached
Boric acid	1.6	2.0 (0.12)	0.02	20.2 (6.2)	—
	11.2	11.3 (0.70)	0.12	0.1 (0.2)	
	22.4	28.5 (1.76)	0.31	0.4 (0.1)	
	44.8	55.5 (3.43)	0.60	1.7 (0)	
Aminoborate 1	1.4	1.4 (0.21)	0.02	2.1 (1.1)	8.0 (3.2)
	9.6	10.2 (1.51)	0.11	1.6 (1.9)	1.9 (0.3)
	19.2	20.7 (3.08)	0.22	2.5 (0.2)	2.4 (0.2)
	38.4	42.7 (6.37)	0.46	3.2 (0.2)	3.2 (0.3)
Aminoborate 2	1.4	1.4 (0.23)	0.02	12.6 (1.7)	34.7 (2.1)
	9.6	10.1 (1.64)	0.11	1.4 (0.2)	36.5 (5.1)
	19.2	20.4 (3.33)	0.22	2.1 (0.2)	39.8 (3.6)
	38.4	42.4 (6.91)	0.46	3.1 (0.6)	42.0 (3.9)
Aminoborate 3	1.4	1.5 (0.30)	0.02	0.7 (0.4)	30.8 (5.4)
	9.9	10.3 (2.12)	0.11	0.6 (0.3)	26.1 (2.0)
	19.8	21.1 (4.32)	0.23	0.9 (0.4)	2.1 (2.1)
	39.7	43.6 (8.95)	0.47	0.7 (0.2)	0 (0)
Aminoborate 4	1.4	1.5 (0.30)	0.02	19.0 (2.5)	37.2 (5.4)
	9.9	10.4 (2.07)	0.11	0.6 (0.1)	15.1 (3.0)
	19.8	21.4 (4.25)	0.23	1.0 (0.1)	0.7 (0.8)
	39.7	44.4 (8.83)	0.48	1.0 (0.2)	0 (0)
Control				27.4 (2.6)	
Solvent (DMF)				23.7 (1.8)	

[a] Values in parentheses are weight percent, average of five replicates
[b] Values in parentheses are standard deviations
[c] Blocks treated with DMF alone and dried at 105°C for 2 da

for leached aminoborate 4 and 3 were 18 mmol and 22.5 mmol/100 g wood, respectively. Aminoborate 2 was ineffective after leaching.

White-rot fungus. Weight losses of aminoborate-treated sweet gum wood decayed by *T. versicolor* are shown in Table 4. For sweet gum wood impregnated with aminoborate 1, threshold retention with *T. versicolor* was below 1.4 mmol/100 g wood for nonleached and leached blocks. Weight losses were 0.6 and 0.8% with retention of 1.4 mmol/100 wood, respectively, for nonleached and leached wood. Leaching did not decrease decay resistance. For aminoborate 2, threshold retention was below 1.4 mmol/100 g wood for nonleached blocks. Weight loss was 1.5% for nonleached wood but was ineffective after leaching. For aminoborate 3, threshold retention was below 1.5 mmol/100 g wood for nonleached wood. Weight loss was 0.9% at retention of 1.5 mmol/100 g wood for nonleached blocks. For leached wood, threshold retention with *T. versicolor* was 39.7 mmol/100 g wood. Weight loss was 0.3% at retention of 43.7 mmol/100 g wood for leached wood. Leaching decreased decay resistance. For aminoborate 4, threshold retention was below 1.4 mmol/100 g wood for nonleached blocks. Weight loss was 1.9% at retention of 1.4 mmol/100 g wood for nonleached wood. For leached wood, threshold retention was 36 mmol/100 g wood. Weight loss was 0% at retention of 44.4 mmol/100 g wood. Leaching greatly decreased decay resistance. The control had 32.3% weight loss, and blocks treated with solvent DMF alone had 28.5% weight loss. Blocks treated with solvent alone required to dry at 105°C for 2 da to avoid the effect of solvent on decay tests.

The above decay tests showed that aminoborates in sweet gum wood without water leaching were as effective as boric acid in preventing decay by *T. versicolor*. For non-leached blocks, threshold retention was below 1.4 mmol/100 g wood, whereas for boric acid, threshold retention was

TABLE 4. *Effect of aminoborates on weight losses of sweet gum blocks decayed by* Trametes versicolor *in a 12-wk soil-block fungal decay test.*

Treatment	Solution Concentration (mmol/100 g solution)	Chemical retention (mmol/100 g wood)[a]	Boron content (% solution)	Weight loss (%)[b] by *Tv*	
				Non-leached	Leached
Boric acid	1.6	2.0 (0.12)	0.02	0.2 (0.1)	—
	11.2	11.4 (0.71)	0.12	0.2 (0.3)	
	22.4	22.8 (1.41)	0.31	0.5 (0.2)	
	44.8	56.0 (3.41)	0.60	1.9 (0.3)	
Aminoborate 1	1.4	1.4 (0.21)	0.02	0.6 (0.4)	0.8 (0.5)
	9.6	10.2 (1.52)	0.11	0.7 (0.2)	1.1 (0.2)
	19.2	20.6 (3.06)	0.22	1.6 (0.4)	1.7 (0.3)
	38.4	42.4 (6.32)	0.46	1.9 (0.6)	1.5 (0.5)
Aminoborate 2	1.4	1.4 (0.23)	0.02	1.5 (0.8)	32.0 (3.9)
	9.6	10.0 (1.63)	0.11	0.9 (0.2)	35.0 (6.3)
	19.2	20.4 (3.33)	0.22	0.9 (0.2)	38.8 (5.3)
	38.4	42.1 (6.86)	0.46	0.7 (0.1)	32.8 (5.4)
Aminoborate 3	1.4	1.5 (0.30)	0.02	0.9 (0.3)	42.6 (2.1)
	9.9	10.3 (2.11)	0.11	0.6 (0.1)	52.0 (4.8)
	19.8	21.1 (4.32)	0.23	1.0 (0.2)	36.9 (5.6)
	39.7	43.7 (9.00)	0.47	1.1 (0.2)	0.3 (0.4)
Aminoborate 4	1.4	1.4 (0.30)	0.02	1.9 (0.7)	36.3 (4.7)
	9.9	10.4 (2.07)	0.11	1.1 (0.3)	32.7 (3.6)
	19.8	21.4 (4.25)	0.23	1.2 (0.1)	6.9 (2.8)
	39.7	44.4 (8.83)	0.48	1.5 (0.3)	0 (0)
Control				32.3 (4.7)	
Solvent (DMF)[c]				28.5 (4.2)	

[a] Values in parentheses are weight percent, average of five replicates.
[b] Values in parentheses are standard deviation.
[c] Blocks treated with DMF (N, N-dimethyl formamide) alone and dried at 105°C for 2 da.

below 2 mmol/100 g wood. For aminoborate 1, leaching did not decrease the decay resistance with threshold retention below 1.4 mmol/100 g wood. Aminoborate 3 and 4 after leaching had significantly decreased decay resistance, threshold retentions were 39.7 and 36 mmol/100 g wood respectively for aminoborate 3 and 4. Aminoborate 2 was ineffective after leaching.

Weight loss was higher for the high retentions than the low retentions for boric acid and aminoborate 1 decayed by *G. trabeum* and *T. versicolor*, which may be attributed to the hydrolysis of boric acid and aminoborate 1 during 12-wk decay tests. This operational loss was also reported for pentachlorophenol using petroleum as a solvent in decay tests.

Thermal degradation

TGA analysis. TGA of wood in the presence of fire retardants has been used to evaluate the effectiveness of fire retardant to protect wood from thermal degradation (Shafizadeh and Sekiguchi 1984). Char yield at 500 or 600°C in nitrogen has been shown to correlate well with fire-retardant efficacy in wood products treated with fire retardants (Shafizadeh et al 1975). The char yields of wood treated with aminoborates at 500°C in nitrogen (Table 5) were compared with those of wood treated with known fire retardants including diammonium phosphate and boric acid.

TABLE 5. *Char yields of wood impregnated with aminoborates, diammonium phosphate or boric acid at 500°C in nitrogen by* TGA.

Treatment (100 mmol/100 g wood)	Char yield (%)
Diammonium phosphate (DAP)	44.0
Aminoborate 1	37.4
Aminoborate 2	33.6
Aminoborate 3	24.6
Aminoborate 4	37.3
Boric acid	32.0
Southern pine (Control)	24.6

The results of TGA analysis (Table 5) indicated that wood treated with aminoborate 1 and 4 have high char yields of 37.4 and 37.3%, respectively. Char yields for boric acid and diammonium phosphate were 32 and 44%, respectively. Aminoborate 1 and 4 provided good fire retardancy to wood.

DSC analysis. Pyrolysis of wood components and wood in nitrogen between 50 and 500°C by DSC in our previous study (Lee et al 2004a) (Fig 5) showed that among wood components, xylan had the lowest thermal stability and decomposed at 150°C. For cellulose, pyrolysis started at 340°C with depolymerization, decomposition, and volatile formation followed by two large exothermic reactions (peak at 380 and 425°C) attributed to aliphatic and aromatic char pyrolysis (Shafizadeh et al 1983). Pyrolysis of lignin was slow at 200–350°C, and active pyrolysis started at 350°C with exothermic reactions. Pyrolysis of wood was influenced by its components, which started with early decomposition of hemicelluloses, slow pyrolysis of lignin, and then depolymerization of cellulose, followed by active pyrolysis of aliphatic and aromatic chars (Fig 5).

Pyrolysis of cellulose plays an important role in wood pyrolysis. Pyrolysis of cellulose proceeds by two pathways. Below 300°C or in the presence of phosphorus fire retardants, pyrolysis proceeds by dehydration to produce fewer volatile compounds and more char, and above 300°C proceeds by depolymerization to produce more volatile compounds and less char (Fig 6) (Shafizadeh et al 1982).

Pyrolysis of wood in the presence of diammonium phosphate proceeds by dehydration of cellulose and produces fewer volatile compounds and more char (Granzow 1978; Shafizadeh et al 1982, 1983; Shafizadeh and Sekiguchi 1984). The endothermic peak attributed to dehydration of cellulose became very small and appeared at lower temperature (200°C). The exothermic reactions attributed to pyrolysis of char appeared at two temperature regions. The peak temperature at 265°C was attributed to pyrolysis of aliphatic chars, and the peak temperature at 370°C was attributed to pyrolysis of aromatic chars (Fig 7) (Shafizadeh et al 1983; Kur et al 1986; Pastorova et al 1994). Phosphorus compounds can form thermally stable bonds with cellulose during pyrolysis (Langeley et al 1980; Shafizadeh and Sekiguchi 1984). The high char yields along with thermally stable chars indicated that diammoniumphosphate is a good fire retardant for wood products.

Pyrolysis of wood treated with aminoborates in nitrogen was similar to that of boric acid; it proceeds by depolymerization of cellulose, followed by active pyrolysis of aliphatic and aromatic chars (Figs 7, 8). This pathway is similar

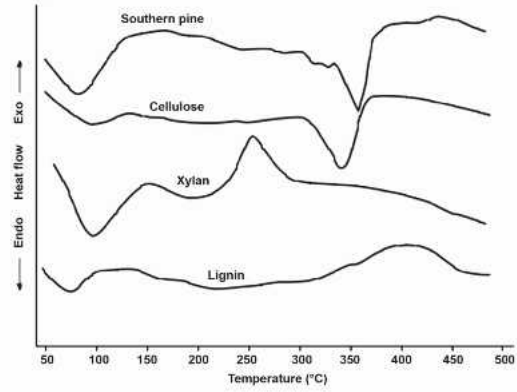

FIGURE 5. DSC analysis in nitrogen of wood and wood components.

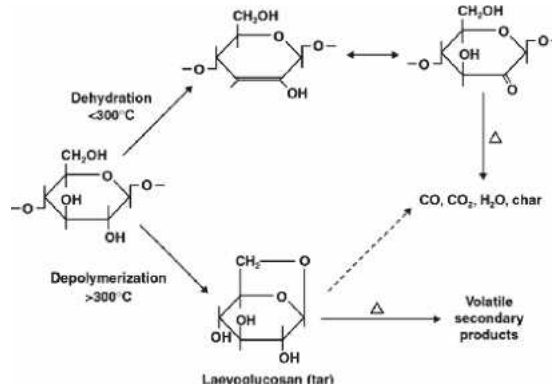

FIGURE 6. Pyrolysis pathways of cellulose.

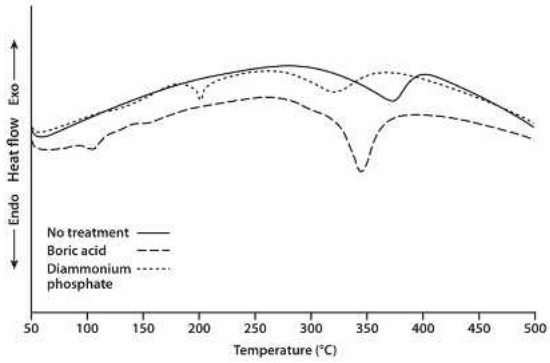

FIGURE 7. DSC in nitrogen of pine wood, and pine wood impregnated with boric acid and diammonium phosphate.

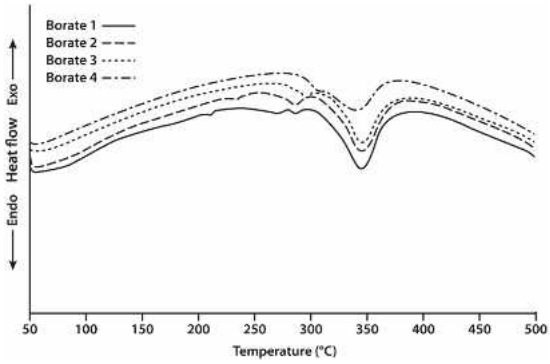

FIGURE 8. DSC in nitrogen of pine wood impregnated with aminoborate 1, 2, 3 and 4.

to the pathway of high temperature pyrolysis of wood as shown in Fig 6 (Shafizadeh et al 1982) which produced more volatile compounds and less char. However, char yields for wood treated with aminoborates or boric acid were high compared with that of high temperature pyrolysis. This indicated that chars formed from wood treated with aminoborates were more stable to thermal degradation (Langeley et al 1980; Shafizadeh et al 1982). Aminoborates are similar to diammonium phosphate in wood which are able to form thermally stable chars in wood during pyrolysis, (Langeley et al. 1980) but the pathways are different.

CONCLUSIONS

Aminoborate 1, 3, and 4 impregnated in wood were more resistant to water leaching than aminoborate 2, and were able to prevent wood from decay by brown- and white-rot fungi. Aminoborate 1 in wood after 2-wk water leaching remained effective against a brown- and white-rot fungus at low chemical retentions. Threshold retention for aminoborate 1 with *G. trabeum* was 9.6 mmol/100 g wood and with *T. versicolor* was below 1.4 mmol/100 g wood.

Char yield by TGA analysis in nitrogen at 500°C showed the following decreasing order:

Diammonium phosphate
> aminoborate 1 > aminoborate 4
> aminoborate 2 > boric acid
> aminoborate 3
= southern pine (control)

DSC showed that the pyrolysis pathway of wood treated with aminoborates was similar to that of wood treated with boric acid which proceeds by depolymerization of cellulose. The depolymerization of cellulose in wood produced less char and more volatile compounds, but char yields of wood treated with aminoborates remained high, which indicated that chars formed from wood impregnated with aminoborates are more stable to thermal degradation.

In our continuous investigations of aminoborates for fungal decay protection in wood products, we were able to synthesize dialkyl aminoborates from reaction of dialkyl amines including dihexyl amine and dioctyl amine with boric acid. These dialkyl aminoborates in wood are more stable and more leach-resistant than the aminoborates reported in this study and performed well in the laboratory fungal decay tests. The hydrophobic dialkyl groups in dialkyl aminoborates play an important role in stability of the compounds and resistance to water leaching. More research is needed to make aminoborates more stable to water leaching and hydrolysis that can be used in exterior applications for wood products.

ACNOWLEDGMENTS

FTIR and NMR analyses were provided by the analytical unit of the Forest Products Laboratory

(FPL), and soil-block fungal decay tests were performed by Rebecca Schumann of FPL.

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